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Dynamic ultrasound scattering analysis of particle dynamics with competing diffusive motion and hydrodynamic interactions

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1. Introduction

Nanoparticles dispersed in liquid exhibit diffusive motion which is well-known to Brownian motion. On the other hand, large micrometer-sized particles settle down due to the mass gravity where the velocity fluctuates around its mean due to long-ranged hydrodynamic interactions. This fluctuation is completely different from the Brownian motion. Note that such long-ranged hydrodynamic interactions are important not only in sedimentation but also in the concentrated nanoparticle suspensions.

Dynamic particle sizing method utilizing the particle motion, such as the dynamic light scattering (DLS) is an effective technique to evaluate the particle diameter in liquid. The particle diameter is obtained by examining the relaxation time of an exponential function representative of diffusion motion. However, in the case of large particles, the time decay exhibits completely different relaxation behavior, resulting in the relaxation is no longer simple exponential relaxation as can be seen in the conventional DLS analysis.

Thus, it is necessary to establish the analysis method which considers both the diffusion motion and the velocity fluctuation accompanying hydrodynamic interactions. Because the wavelength of MHz ultrasound is longer than that of light, ultrasound could be the most suitable method to study such different types of particle motion.

The purpose of this study is to investigate origin of velocity fluctuations with hydrodynamic interactions and to establish the analysis method to utilize ultrasound in the wide range of particle-size from nanometer to micrometer regime without dilution of sample.

2. Experimental section

Fig. 1 schematically shows the setup of the dynamic ultrasonic scattering (DSS) method. Electrically excited pulses of –300 V spikes are irradiated to a 20 or 30 MHz longitudinal ultrasonic transducer. The same transducer was used to receive the echoes. A disposal polystyrene rectangular cell with a path length of 10 mm and a thickness of 1 mm was used as the sample cell. As shown in Fig. 1, particle scattering should be observed between the two echoes, which correspond to the reflected waves from the cell wall. Unless otherwise stated, the sample height was 40 mm. Such scattered waves are acquired at the pulse repetition time of 10 ms, for example. By analyzing the autocorrelation function at a fixed pulse time, the particles motion at a pulse time, i.e., corresponding location in the sample, can be obtained.

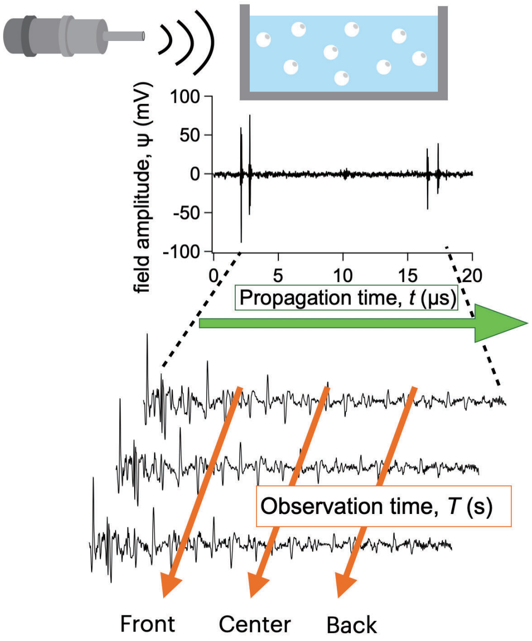

Fig. 1 Schematic representation of the dynamic ultrasound scattering (DSS) method.

3. Result and discussion

Fig. 2 shows examples of the correlation function obtained for a 2.5wt% silica particle of 50 nm diameter, a 1wt% polydivinylbenzene (PDVB) particle of 20 μm diameter and a 5wt% silica particle of 500 nm diameter. Taking the natural logarithm of the correlation function and plotting both logarithms, the exponent of the delay time was confirmed to be 1, 2 and crossover from 1 to 2. This indicates that the particle motion is a Brownian motion with $\langle x^2 \rangle = 2D\tau$ for nanoparticles, a velocity fluctuation with hydrodynamic interaction of $\langle x^2 \rangle = \Delta V^2 \tau^2$ for micron-particles and intermediate between

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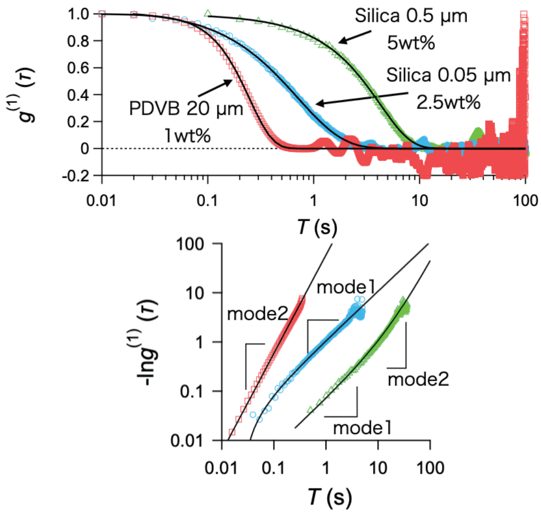

Fig. 2 (a) Time correlation functions obtained for the silica and polydivinylbenzene (PDVB) particles with different particle sizes. (b) Natural log plot of the correlation functions. By multiplying the natural logarithm of the PDVB 20 μm correlation function by 5, the vertical axis is shifted to make the graph easier to read.

Brownian motion and hydrodynamic interaction, i.e., the competition with two types of motions[1,2].

In the DSS analysis, the time-correlation function can be given as a function of the sample position. Thus, the velocity fluctuation could be quantitatively obtained by the corresponding position. The average velocity fluctuations were formulated by Caflisch and Luke (CF)[3] as follows :

$$\Delta V = C_x V_0 \sqrt{\frac{2\phi L}{d}}$$

where ΔV is the standard deviation of velocity, ϕ is the volume fraction, L is the sample path length, and d is the particle diameter, V_0 is the terminal velocity. The physical meaning of the velocity fluctuation is given by Hinch who explains the fluctuating particles move together owing to the long-range nature of the hydrodynamic interactions[4]. This motion is modeled as a blob concept. The number of particles inside each blob can change during sedimentation, and velocity fluctuation is invoked by the number fluctuation of particle inside blob. Since the proportional constant C_x along the horizontal x-axis is unknown, a particle size analysis is not straightforward unlike diffusion measurements (Brownian motion). Therefore, in this study, the cell constant C_x was investigated by analyzing standard particles with known particle sizes, followed by complicated submicron-particle analysis.

Fig. 3 shows the diameter dependence of C_x. When d was several tens of micrometer, C_x was a constant around 0.1. However, C_x increased with decreasing d. The decrease in C_x with increasing d is ascribed to the breaking the blob structure due to concentration gradient caused by the large particle stratification. It was suggested that similar breaking of structure was also found in the submicron particle.

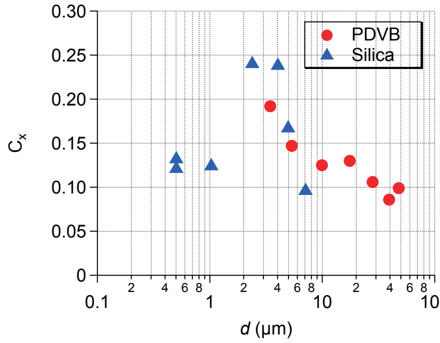

Fig. 3 d dependence of C_x obtained for the PDVB and silica particles.

4. Conclusion

For nanoparticles and micron particles, Brownian motion and hydrodynamic fluctuations were respectively measured by the DSS method. In this study, unknown proportional constant C_x of velocity fluctuation was investigated by changing various parameters such as the density, diameter, and concentration of particle, as well as the cell size. In previous study, C_x was evaluated to be constant up to several tens of micrometers regardless of kind of particle, and C_x increased as the particle diameter becomes smaller. The value of C_x was also determined for the submicron particles.

Velocity fluctuation of submicron size can be quantitatively analyzed by taking account of both diffusive and hydrodynamic fluctuations simultaneously. In this particle size range, C_x indicated similar value to micron size particles. Now, the DSS technique can probe particle dispersion at all the range of particle size from nano to micron by considering Brownian motion, hydrodynamic interaction, or both.

References

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